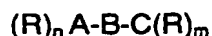


1. A process for polymerising olefins to branched polyolefins by contacting at least one olefin with a combination of catalysts comprising

- (a) a polymerisation catalyst; and
- (b) at least one co-catalyst in the form of an ethylene tetramerisation catalyst to produce 1-octene from ethylene which co-catalyst includes the combination of
 - a transition metal compound; and
 - a heteroatomic ligand described by the general formula



wherein

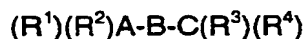
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different, and each R is independently selected from any homo or hetero hydrocarbyl group; and

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of a hydrocarbyl group, a heterohydrocarbyl group, a substituted hydrocarbyl group and a substituted heterohydrocarbyl group; R^1 , R^2 , R^3 and R^4 being characterised therein that either

- (i) any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron-donating; and where R^1 , R^2 , R^3 and R^4 are independently aromatic, including heteroaromatic groups, not all the groups R^1 ,

- R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C; or
- (ii) at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent on a second or further atom from the atom bound to A or C and provided that any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bound to A or C.
2. The process as claimed in claim 1 wherein the olefin is ethylene and the branched polyolefin is a branched polyethylene.
3. The process as claimed in claim 1 or claim 2 wherein the branched polyolefin is linear low density polyethylene.
4. The process as claimed in any one of the preceding claims, wherein the heteroatomic ligand of the co-catalyst is described by the general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth, and nitrogen; B is a linking group between A and C; and R^1 to R^4 are independently selected from the group consisting of a hydrocarbyl group, a heterohydrocarbyl group, and a substituted heterohydrocarbyl group, R^1 to R^4 being characterised therein that either
- (i) any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron-donating; and where R^1 , R^2 , R^3 and R^4 are independently aromatic, including heteroaromatic groups, not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C; or
- (ii) at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent on a second or further atom from the atom bound to A or C and provided that any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bound to A or C.
5. The process as claimed in claim 4 wherein R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of a non-aromatic group, and an aromatic group, including a heteroaromatic group.

6. The process as claimed in claim 5 wherein each of R^1 , R^2 , R^3 and R^4 is independently an aromatic, including a heteroaromatic group and not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C.
7. The process as claimed in claim 6 wherein not more than two of R^1 , R^2 , R^3 and R^4 have substituents on the atom adjacent to the atom bound to A or C.
8. The process as claimed in any one of claims 4 to 7 wherein any polar substituent on one or more of R^1 , R^2 , R^3 and R^4 is electron-donating.
9. The process as claimed in any one of claims 4 to 7 wherein each non-electron donating substituent is non-polar.
10. The process as claimed in any one of claims 1 to 9 wherein B is selected from the group consisting of an organic linking group comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; an inorganic linking group comprising a single atom linking spacer; and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is selected from the group consisting of hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom, a halogen, a cyclic heteroatomic group or a cyclic homoatomic group.
11. The process as claimed in claim 10 wherein B is a single atom linking spacer.
12. The process as claimed in claim 10, wherein B is $-N(R^5)-$, wherein R^5 is hydrogen or selected from the group consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, aryl substituted with any of these substituents, and any cyclic heteroatomic group including cyclopentadienyl dimethylsilyl-t-butylamidato or a cyclic homoatomic group including cyclopentadienyl, indenyl and fluorene.
13. The process as claimed in any one of claims 1 to 12, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.

14. The process as claimed in any one of claims 1 to 12, wherein A and/or C is independently phosphorus.
15. The process as claimed in claim 4, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group consisting of a benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and a tetrahydrofuranyl group.
16. The process as claimed in claim 4 wherein R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of a phenyl, tolyl, biphenyl, naphthyl, thiophenyl and ethyl group.
17. The process as claimed in claim 1 or claim 4, wherein the heteroatomic ligand is selected from the group consisting of
- | | |
|---|---|
| (phenyl) ₂ PN(methyl)P(phenyl) ₂ , | (phenyl) ₂ PN(pentyl)P(phenyl) ₂ , |
| (phenyl) ₂ PN(phenyl)P(phenyl) ₂ , | (phenyl) ₂ PN(p-methoxyphenyl)P(phenyl) ₂ , |
| (phenyl) ₂ PN(p-butylphenyl)P(phenyl) ₂ , | (phenyl) ₂ PN((CH ₂) ₃ -N-morpholine)P(phenyl) ₂ , |
| (((phenyl) ₂ P) ₂ NCH ₂ CH ₂) ₃ N, | (phenyl) ₂ PN(Si(CH ₃) ₃)P(phenyl) ₂ , |
| (ethyl) ₂ PN(isopropyl)P(phenyl) ₂ , | (ethyl) ₂ PN(methyl)P(ethyl) ₂ , |
| (ethyl)(phenyl)PN(methyl)P(ethyl)(phenyl), | (ethyl)(phenyl)PN(isopropyl)P(phenyl) ₂ , |
| (phenyl) ₂ P(=Se)N(isopropyl)P(phenyl) ₂ , | (phenyl) ₂ PCH ₂ CH ₂ P(phenyl) ₂ , |
| (o-ethylphenyl)(phenyl)PN(isopropyl)P(phenyl) ₂ , | (o-methylphenyl) ₂ PN(isopropyl)P(o-methylphenyl)(phenyl), |
| (phenyl) ₂ PN(benzyl)-P(phenyl) ₂ , | (phenyl) ₂ PN(1-cyclohexylethyl)P(phenyl) ₂ , |
| (phenyl) ₂ PN[CH ₂ CH ₂ CH ₂ Si(OMe) ₃]P(phenyl) ₂ , | (phenyl) ₂ PN(cyclohexyl)P(phenyl) ₂ , |
| (phenyl) ₂ PN(2-methylcyclohexyl)P(phenyl) ₂ , | (phenyl) ₂ PN(allyl)P(phenyl) ₂ , |
| (o-naphthyl) ₂ PN(methyl)P(o-naphthyl) ₂ , | (p-biphenyl) ₂ PN(methyl)P(p-biphenyl) ₂ , |
| (p-Me-phenyl) ₂ PN(methyl)P(p-Me-phenyl) ₂ , | (o-thiophenyl) ₂ PN(methyl)P(o-thiophenyl) ₂ , |
| (phenyl) ₂ PN(methyl)N(methyl)P(phenyl) ₂ , | (m-Me-phenyl) ₂ PN(methyl)P(m-Me-phenyl) ₂ , |
| (phenyl) ₂ PN(isopropyl)P(phenyl) ₂ , | |

(phenyl)₂P(=S)N(isopropyl)P(phenyl)₂, and
 (phenyl)₂P(=S)N(isopropyl)P(=S)(phenyl)₂.

18. The process as claimed in claim 1 or 4, wherein the heteroatomic ligand is selected from the group consisting of ((*m*-methoxyphenyl)₂PN(methyl)P(*m*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(methyl)P(*p*-methoxyphenyl)₂, (*m*-methoxyphenyl)₂PN(isopropyl)P(*m*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(isopropyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(2-ethylhexyl)P(*p*-methoxyphenyl)₂, (*m*-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂ and (*p*-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂, (*p*-methoxyphenyl)(phenyl)PN(methyl)P(*m*-methoxyphenyl)(phenyl), (*p*-methoxyphenyl)(phenyl)PN(methyl)P(*p*-methoxyphenyl)(phenyl), (*m*-methoxyphenyl)₂PN(methyl)P(phenyl)₂ and (*p*-methoxyphenyl)₂PN(methyl)P(phenyl)₂, (*p*-methoxyphenyl)₂PN(1-cyclohexylethyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(2-methylcyclohexyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(decyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(pentyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(benzyl)P(*p*-methoxyphenyl)₂, (*p*-methoxyphenyl)₂PN(phenyl)P(*p*-methoxyphenyl)₂, (*p*-fluorophenyl)₂PN(methyl)P(*p*-fluorophenyl)₂, (*o*-fluorophenyl)₂PN(methyl)P(*o*-fluorophenyl)₂, (*p*-dimethylamino-phenyl)₂PN(methyl)P(*p*-dimethylamino-phenyl)₂, (*p*-methoxyphenyl)₂PN(allyl)P(*p*-methoxyphenyl)₂, (*p*-(*p*-methoxyphenyl)-phenyl)₂PN(isopropyl)P(*p*-(*p*-methoxyphenyl)-phenyl)₂ and (*p*-methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)₂.
19. The process as claimed in any one of the preceding claims wherein the polymerisation catalyst is selected from the group consisting of a Ziegler-Natta catalyst, an unbridged metallocene, a half sandwich metallocene, a carbon-bridged metallocene and a silyl-bridged metallocene.
20. The process as claimed in claim 19, wherein the Ziegler-Natta catalyst is selected from the group consisting of TiCl₃-Et₂AlCl, AlR₃-TiCl₄.
21. The process as claimed in claim 19, wherein the unbridged metallocene is selected from the group consisting of:
 bis(cyclopentadienyl)chromium(II),

bis(cyclopentadienyl)-zirconium Chloride hydride,
 bis(cyclopentadienyl)-titanium dichloride,
 bis(cyclopentadienyl)-zirconium dichloride,
 bis(cyclopentadienyl)-zirconium dimethyl,
 bis(*n*-butylcyclopentadienyl)-zirconium dichloride,
 bis(*n*-dodecylcyclopentadienyl)-zirconium dichloride,
 bis(ethylcyclopentadienyl)-zirconium dichloride,
 bis(iso-butylcyclopentadienyl)-zirconium dichloride,
 bis(isopropylcyclopentadienyl)-zirconium dichloride,
 bis(methylcyclopentadienyl)-zirconium dichloride,
 bis(*n*-octylcyclopentadienyl)-zirconium dichloride,
 bis(*n*-pentylcyclopentadienyl)-zirconium dichloride,
 bis(*n*-propylcyclopentadienyl)-zirconium dichloride,
 bis(trimethylsilylcyclopentadienyl)-zirconium dichloride,
 bis(1,3-bis(trimethylsilyl)cyclopentadienyl)-zirconium dichloride,
 bis(1-ethyl-3-methylcyclopentadienyl)-zirconium dichloride,
 bis(pentamethylcyclopentadienyl)-zirconium dichloride,
 bis(pentamethylcyclopentadienyl)-zirconium dimethyl,
 bis(1-propyl-3-methylcyclopentadienyl)-zirconium dichloride,
 bis(4,7-dimethylindenyl)-zirconium dichloride,
 bis(indenyl)-zirconium dichloride,
 bis(2-methylindenyl)-zirconium dichloride,
 bis(2-methylindenyl)-zirconium dichloride, and
 cyclopentadienylindenyl-zirconium dichloride.

22. The process as claimed in claim 19, wherein the half sandwich metallocene is selected from the group consisting of:

cyclopentadienyl-zirconium trichloride,
 pentamethylcyclopentadienyl titanium trichloride,
 pentamethylcyclopentadienyl-titanium Trimethoxide,
 pentamethylcyclopentadienyl-titanium Trimethyl,
 pentamethylcyclopentadienyl-zirconium trichloride,
 tetramethylcyclopentadienyl-zirconium trichloride, and
 1,2,4-trimethylcyclopentadienyl-zirconium trichloride.

23. The process as claimed in claim 19, wherein the carbon-bridged metallocene is selected from the group consisting of:

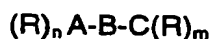
diphenylmethylidene(cyclopentadienyl)-(9-fluorenyl)-zirconium dichloride,
 diphenylmethylidene(cyclopentadienyl)-(indenyl)-zirconium dichloride,
 iso-propylidenebis(cyclopentadienyl)-zirconium dichloride,
 iso-propylidene(cyclopentadienyl)(9-fluorenyl)-zirconium dichloride, and
 iso-propylidene(3-methylcyclopentadienyl)-(9-fluorenyl)-zirconium dichloride.
 ethylene-bis(9-fluorenyl)-zirconium dichloride,
meso-ethylene-bis(1-indenyl)-zirconium dichloride,
rac-ethylene-bis(1-indenyl)-zirconium dichloride,
rac-ethylene-bis(1-indenyl)-zirconium dimethyl,
rac-ethylene-bis(2-methyl-1-indenyl)-zirconium dichloride, and
rac-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)-zirconium dichloride

24. The process as claimed in claim 19, wherein the silyl-bridged metallocene is selected from the group consisting of:
 dimethylsilyl-bis(cyclopentadienyl)-zirconium dichloride,
 dimethylsilyl-bis(9-fluorenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(1-indenyl)-zirconium dichloride,
meso-dimethylsilyl-bis(2-methylindenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(2-methylindenyl)-zirconium dichloride,
rac-dimethylsilyl-bis(tetrahydroindenyl)-zirconium dichloride,
 dimethylsilyl-bis(tetramethylcyclopentadienyl)-zirconium dichloride,
 diphenylsilyl(cyclopentadienyl)(9-fluorenyl)-zirconium dichloride, and
 diphenylsilyl-bis(indenyl)hafnium dichloride.
25. The process as claimed in any one of the preceding claims, wherein branched polymers in the form of polyolefins are formed by means of a tandem tetramerisation due to the co-catalyst and a polymerisation process due to the polymerisation catalyst.
26. The process as claimed in claim 25, the tandem tetramerisation and polymerisation process is an *in situ* catalysis process wherein tetramerisation and polymerisation takes place in the same reaction medium.
27. The process as claimed in claim 26, wherein the *in situ* catalysis process is an in-situ concurrent catalysis process.

28. The process as claimed in claim 26, wherein the *in situ* catalysis process is an *in situ* consecutive catalysis process.
29. The process as claimed in claim 26 wherein the olefin in the form of ethylene is tetramerised using the co-catalyst to produce 1-octene and the 1-octene is copolymerized *in situ* with ethylene using the polymerisation catalyst.
30. The process as claimed in claim 29 wherein the polymerisation catalyst includes a transition metal.
31. The process as claimed in any one of claims 1 to 30, which includes the step of combining the heteroatomic ligand with the transition metal compound and an activator in the presence of the polymerisation catalyst.
32. The process as claimed in claim 31, wherein the transition metal of the transition metal compound is selected from the group consisting of chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
33. The process as claimed in claim 32, wherein the transition metal of the transition metal compound is chromium.
34. The process as claimed in any one of claims 1 to 33, wherein the transition metal compound of the co-catalyst is selected from the group consisting of an inorganic salt, an organic salt, a coordination complex and organometallic complex.
35. The process as claimed in claim 34, wherein the transition metal compound is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex, (benzene)-tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.
36. The process as claimed in claim 35, wherein the transition metal compound is selected from the group consisting of chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.

37. The process as claimed in any one of claims 1 to 36, wherein the transition metal of the transition metal compound and the heteroatomic ligand are combined to provide a transition metal/ligand molar ratio from about 0.01:100 to 10 000:1.
38. The process as claimed in any one of claims 1 to 37, wherein the co-catalyst includes an activator selected from the group consisting of an organoaluminium compound, an organoboron compound, an organic salt, an inorganic acid and an inorganic salt.
39. The process as claimed in claim 38, wherein the activator is an alkylaluminoxane.
40. The process as claimed in claim 39, wherein the transition metal of the transition metal compound of the co-catalyst and the aluminoxane are combined in a proportion to provide an Al/transition metal molar ratio from about 1:1 to 10 000:1.
41. The process as claimed in any one of claims 1 to 40, wherein the heteroatomic ligand and the transition metal compound of the co-catalyst are combined at any temperature between -20°C and 250°C in the presence of the olefin.
42. The process as claimed in any one of claims 1 to 41, wherein the co-catalyst and polymerisation catalyst are combined in the molar ratio of 0.01:100 to 10000:1.
43. The process as claimed in any one of the preceding claims, which is carried out in an inert solvent.
44. The process of any one of the preceding claims wherein the olefin is ethylene which is contacted with the combination of catalysts at a pressure of more than 100 kPa (1 barg).
45. The process as claimed in any one of the preceding claims, wherein the polymerisation catalyst and the co-catalyst are mixed at any temperature between -20°C and 250°C in the presence of the olefin.

46. The process as claimed in any one of the proceeding claims where the process is carried out in a combination of reactors, the first reactor being a continuous stirred tank reactor and the second reactor being selected from the group consisting of a batch reactor, a continuous stirred tank reactor and a plug flow reactor.
47. A catalyst combination comprising
- (a) a polymerisation catalyst; and
 - (b) at least one co-catalyst in the form of an ethylene tetramerisation catalyst to produce 1-octene from ethylene which co-catalyst includes the combination of
 - a transition metal compound; and
 - a heteroatomic ligand described by the general formula



wherein

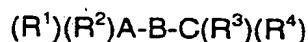
A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium and nitrogen;

B is a linking group between A and C;

the R groups are the same or different, and each R is independently selected from any homo or hetero hydrocarbyl group; and

n and m for each R is independently determined by the respective valence and oxidation state of A and C; and

provided that where the heteroatomic ligand is described by the following general formula



wherein

A and C are independently selected from the group consisting of phosphorus, arsenic, antimony, bismuth and nitrogen;

B is a linking group between A and C; and

R^1 , R^2 , R^3 and R^4 are independently selected from the group consisting of a hydrocarbyl group, a heterohydrocarbyl group,

a substituted hydrocarbyl group and a substituted heterohydrocarbyl group; R^1 , R^2 , R^3 and R^4 being characterised therein that either

- (i) any substituents on one or more of R^1 , R^2 , R^3 and R^4 are not electron-donating; and where R^1 , R^2 , R^3 and R^4 are independently aromatic, including heteroaromatic groups, not all the groups R^1 , R^2 , R^3 and R^4 have a substituent on the atom adjacent to the atom bound to A or C; or
- (ii) at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent on a second or further atom from the atom bound to A or C and provided that any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bound to A or C.